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## PATENT ABSTRACTS OF JAPAN

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(21) Application number : 02-092472 (71) Applicant : DAINIPPON SCREEN MFG CO LTD  
(22) Date of filing : 07. 04. 1990 (72) Inventor : TANAKA MASATO  
NISHIZAWA HISAO

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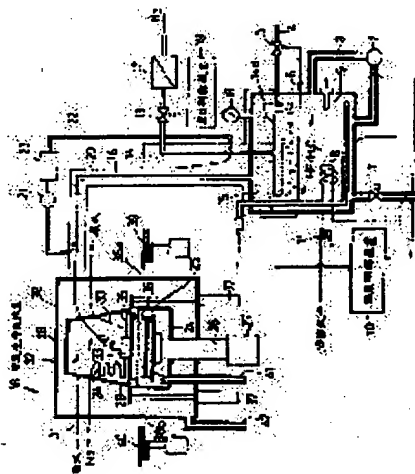
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## (54) CLEANING TREATMENT OF SUBSTRATE AND DEVICE

## (57) Abstract:

PURPOSE: To eliminate an aerosol in the vapor of a cleaning liquid in the cleaning treatment of a substrate by a method wherein the cleaning liquid is evaporated at a temperature lower than its boiling point and the generated vapor of the cleaning liquid is fed to the substrate at a temperature exceeding its dew point to perform the cleaning treatment of the substrate.

CONSTITUTION: Water warmed by a heater 23 to a necessary temperature (such as 50° C) is circulated, the temperature of the vapor of a cleaning liquid, which is the mixed vapor of fluorinated hydrogen gas to be flowed from a vapor storage part 15 to a vapor feed pipe 16 and pure water vapor HF/H<sub>2</sub>O, is maintained at a temperature exceeding the dew point of the vapor and in the vapor of the cleaning liquid obtainable by mixing the fluorinated hydrogen gas with the pure water vapor, the pseudo-azeotropic temperature of the fluorinated hydrogen gas under the conditions of 760mmHg and 30° C is maintained in 39.4%. That is, the vapor of the cleaning liquid in an atmosphere and the saturated vapor pressure of each component in the vapor are respectively set at the respective partial pressures or lower.



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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

A <Field of the Invention> this invention relates to the washing art and washing processor of a substrate.

According to the technology indicated by <Prior-art> JP,62-173720,A \*\* By containing a substrate to the processing interior of a room, and supplying the steam of hydrofluoric-acid HF to \*\* processing interior of a room After dissolving the oxide film on the front face of a substrate, carrying out flowing-down eccrisis and completing removal of an oxide film, stop supply of the steam of \*\* hydrofluoric acid and the steam of a high grade is instead supplied to the processing interior of a room. After flushing the hydrofluoric acid adhering to the substrate front face and the processing indoor wall surface and fully replacing with water, supply of \*\* steam is stopped, the nitrogen gas N<sub>2</sub> of a high grade heated instead is supplied to a processing room, and a substrate is dried.

In this case, the method of heating \*\* depot, the method of bubbling by the entrainment of the nitrogen gas N<sub>2</sub> to the inside of \*\* solution, and the method using \*\* ultrasonic wave radiator are indicated as a method of generating the steam of a hydrofluoric acid from the depot of the solution of hydrofluoric-acid HF.

Moreover, according to the technology indicated by JP,62-213127,A \*\*, supplying the pure nitrogen gas N<sub>2</sub> to the processing interior of a room [ while rotating the substrate contained to the processing interior of a room, and ] \*\* At the same time it supplies the hydrogen fluoride gas HF which heated and obtained the anhydrous hydrofluoric acid to the processing interior of a room Introduce fog-like ultrapure water into the processing interior of a room, generate a hydrofluoric acid by hydrogen fluoride HF and ultrapure water, and the oxide film on a substrate is removed by the hydrofluoric acid. \*\* Injection of ultrapure water washes a substrate front face, where the \*\* nitrogen gas N<sub>2</sub> is introduced, carry out high-speed rotation of the substrate, and dry a substrate by the liquid end.

also in the technology of which official report of <Object of the Invention> JP,62-173720,A or JP,62-213127,A, before drying a substrate, the steam of a high grade is supplied to a substrate front face and a processing indoor wall surface, or it is in a substrate un-arranging [ which injects ultrapure water / to which particle remains on a substrate front face in spite of having flushed the substrate especially more ]

In the technology of JP,62-173720,A, aerosol (Myst) occurs with a steam by all of the method of \*\* which generates the steam of hydrofluoric-acid HF - \*\*. That is, when it is \*\*, in \*\*, in \*\*, aerosol occurs by cavitation by boil with gassing, respectively.

Moreover, in the technology of JP,62-213127,A, it becomes adhesion in the substrate of aerosol to supply ultrapure water in the shape of a fog and to melt hydrogen fluoride gas to the ultrapure water of the shape of the fog, and to supply the hydrofluoric acid of a liquid to a direct substrate itself. this invention is made in view of such a situation, and aims at offering effective equipment, when enforcing the method of performing washing processing of a highly precise substrate in which particle is not made to remain, and its method. It aims at there being no impurity and enabling it to etch uniformly by losing aerosol in the steam of washing processing liquid, and specifically, losing aerosol in the

washing processing accompanied by etching in washing processing, for the purpose of avoiding the interface of the gaseous-phase-liquid phase and each gaseous-phase-solid phase, and generation of the colloidal silica in the periphery, and making the front face of a substrate pure.

The experiment which went to the well which finds out a <The-means-for-solving-a-technical-problem> solution means (cause investigation of particle generating)

[Experiment]

Several drops of solution of 25% of hydrogen fluoride is hung down to a silicon wafer front face with ISHIRIKON thermal oxidation film (th-SiO<sub>2</sub>) 5,000Å. And the etching reaction of a thermal oxidation film whose thermal oxidation film observed signs that it \*\*\*\*\*ed, with the optical microscope (refer to the 4th view ) advances to a perpendicular direction and a horizontal direction to a silicon wafer. The reaction to a perpendicular direction is mainly  $6\text{HF} + \text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$ . ..... It is considered \*\*. H<sub>2</sub>SiF<sub>6</sub> is a hexafluorosilicic acid. In addition, especially generating of a foam is not accepted.

The flare of the hydrofluoric acid to a horizontal direction is quick. The thermal oxidation film surface around liquid receives corrosion in the shape of a scale by mixed steamy HF/H<sub>2</sub>O to which a horizontal etching reaction comes out of the drop of a hydrofluoric acid first. The reaction is  $\text{SiO}_2 + 4\text{HF} + 2\text{H}_2\text{O} \rightarrow \text{SiF}_4 + 4\text{H}_2\text{O}$ . ..... It is \*\*. SiF<sub>4</sub> is a silicon tetrafluoride (gas).

And etching by formula \*\* is perpendicularly performed by the hydrofluoric acid which spreads horizontally.

The drop of a hydrofluoric acid was separately hung down to the front face of RO, next the raise in basic waxes silicon which carried out etching removal of the silicon thermal oxidation film completely by mixed steamy HF/H<sub>2</sub>O, and signs that it changed every moment were observed with the optical microscope (refer to the 5th view ).

Since the front face of the raise in basic waxes silicon from which the thermal oxidation film was removed completely is hydrophobic, if a drop is hung down, it will become semi-sphere-like. If it is observing for a while, the deposition of colloidal silica SiO<sub>2</sub> and nH<sub>2</sub>O (colloid silicon oxide) will come to be gradually accepted in the interface of the gaseous-phase-liquid phase and each gaseous-phase-solid phase around a drop.

A drop becomes small gradually and its colloidal silica which carries out deposition to the circumference also increases. In the meantime, suspension of a comparatively big colloidal particle is accepted into a drop.

The size of colloidal silica is about a maximum of 0.625-micrometer particle. thus, the aggregate of the colloidal silica which carried out deposition -- a raise in basic waxes silicon front face -- silverfish -- it becomes a \*\* and the so-called blue haze is produced It is not generated only in the interface of the gaseous-phase-liquid phase and each gaseous-phase-solid phase, but the deposition of colloidal silica is produced on a raise in basic waxes silicon front face also in the circumference which surround a drop. If the drop of a diameter d is hung down on the surface of a silicon wafer as shown in a view 5, in the interface of the gaseous-phase-solid phase of the range of a diameter D (D\*\*4d), colloidal silica will carry out deposition to the circumference of the drop promptly.

Moreover, colloidal silica occurs also in the front face of a drop, i.e., the interface of the gaseous-phase-liquid phase.

The incidence rate of colloidal silica becomes low as it is the highest also in any of the interface of gaseous-phase-solid phase, and the interface of the gaseous-phase-liquid phase and keeps away.

In the interface of the gaseous-phase-solid phase of a view 5, although the cause which colloidal silica generates is not clear, the moisture which evaporates from the drop front face hung down to the wafer front face, and the silicon tetrafluoride in atmosphere join together, and it is thought that colloidal silica occurs.

If a drop is finally lost after the drop decreases gradually and colloidal silica carries out deposition to the circumference of a drop to some extent in connection with this, the big colloidal particle which was floating in the drop will remain in a core. However, if the vapor rate of a drop is sped up, finally colloidal silica will be in the state where deposition was carried out only at the periphery section, and a

colloidal particle will not remain in a core (refer to the 6th view ).

Thus, it is a portion in contact with the atmosphere of etching processing that colloidal silica is generated, and it is not generated in the interface of the portion which was covered by the drop and has got wet, i.e., liquid phase-solid phase.

HA, next the experiment which investigates a relation with the rinse by deionized water (pure water) were conducted.

The waterdrop of pure water was hung down to the front face of raise in basic wages silicon after removing a natural oxidation film by the hydrofluoric acid, and it observed under the microscope. If the waterdrop of pure water is immediately hung down to the front face of raise in basic wages silicon after removal of a natural oxidation film, colloidal silica will generate to the circumference. In the case of the raise in basic wages silicon which removed and carried out the rinse of \*\*\*\*\* and the natural oxidation film, it is hard to generate colloidal silica.

When a silicon front face and various matter, such as carbon in air, join together, it thinks for the activation energy on the front face of silicon to become weak.

Therefore, by the time mixed steamy HF/H<sub>2</sub>O removes a natural oxidation film and the front face of raise in basic wages silicon is being worn with pure water, especially colloidal silica may be generated, and it is thought that it serves as particle.

[Consideration]

Generation of colloidal silica has taken place in the portion exposed to atmosphere among the raise in basic wages silicon front faces after \*\*\*\*\*ing by the hydrofluoric acid. Moreover, colloidal silica was generated around the drop, and the inclination for the incidence rate to decrease was accepted as it kept away from the interface of the gaseous-phase-liquid phase and each gaseous-phase-solid phase.

This shows that there are moisture concentration in atmosphere and a close relation to generating of colloidal silica. Colloidal silica is SiO<sub>2</sub> and nH<sub>2</sub>O, and if it generates, it is thought that the silicon tetrafluoride SiF<sub>4</sub> (gas) generated by processing of a hydrofluoric acid reacts with the moisture in atmosphere like following formula \*\*, and is made.

$3\text{SiF}_4 + 3\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2\text{SiF}_6$  ..... It is thought that it is based on \*\*, i.e., the adding-water decomposition reaction of a silicon tetrafluoride SiF<sub>4</sub> (gas).

The thing generated by \*\* formula as a silicon tetrafluoride, or the thing generated by corroding raise in basic wages silicon by the steam HF which evaporated from the drop of a hydrofluoric acid, Or what hexafluorosilicic-acid H<sub>2</sub>SiF<sub>6</sub> in a drop decomposed like  $\text{H}_2\text{SiF}_6 \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$ , and was generated can be considered, this silicon tetrafluoride SiF<sub>4</sub> and steam H<sub>2</sub>O start the adding-water decomposition reaction of \*\* formula, and it is thought that colloidal silica is generated and carries out deposition.

That one more is considered as a cause of generation of colloidal silica SiO<sub>2</sub> and nH<sub>2</sub>O is possibility of being generated by the silicon which carried out like following formula \*\* and dissolved into the hydrofluoric acid.

$2\text{H}^+ + \text{SiF}_6^{2-} + 6\text{OH}^- \rightarrow \text{SiO}_2 + 6\text{F}^- + 3\text{H}_2\text{O}$  ..... It is the interface of the gaseous-phase-liquid phase which the reaction of \*\*, however \*\* formula produces, and a reaction does not attain to the circumference of a drop.

Therefore, the deposition of colloidal silica is considered to be promoted by the adding-water decomposition reaction by part for atmosphere Nakamizu of the silicon tetrafluoride mainly generated by etching on the front face of silicon by hydrogen fluoride.

Moreover, colloidal silica is promoted by the drop adhering to the front face of the raise in basic wages silicon from which the natural oxidation film was removed. Therefore, if Myst and aerosol adhere to a front face, it becomes a nucleus and generation of colloidal silica will be promoted.

[Conclusion]

(a) The deposition of colloidal silica is promoted by the adding-water decomposition reaction by part for atmosphere Nakamizu of the silicon tetrafluoride generated by etching on the front face of silicon by hydrogen fluoride.

(b) Generate the deposition of colloidal silica around the drop adhering to the raise in basic wages silicon front face on which the natural oxidation film was removed.

- (c) The deposition of colloidal silica is not accepted in the portion covered by the drop.
- (d) After a raise in basic waxes silicon front face becomes carry out etching removal of the natural oxidation film by the hydrofluoric acid, and self-possessed [ colloidal silica ] and hydrophobic, especially by the time a raise in basic waxes silicon front face is exposed to atmosphere and a front face is being worn by deionized water, it will happen.
- (e) The incidence rate of the colloidal silica which carries out deposition to the circumference of a drop falls gradually as it is the highest in the interface of the gaseous-phase-liquid phase and each gaseous-phase-solid phase and keeps away.
- (f) Especially, etching processing and rinse processing are performed continuously and colloidal silica is not generated by the hachures [ make ] which expose a raise in basic waxes silicon front face to the atmosphere, and the raise in basic waxes silicon wafer front face of an activity state.
- (g) the size of colloidal silica -- about 0.625 micrometers -- it is -- a set field -- a naked eye -- silverfish - - it is observed as nonuniformity of a \*\*

In order not to make colloidal silica generate from the above thing, it is making it aerosol (Myst) not included in the atmosphere of a washing process, and, for that, they are not supplying aerosol to a silicon wafer, and the thing the steam of the washing processing liquid supplied to the silicon wafer liquefies, and it is made not to produce aerosol.

This was discovered by this experiment and the means for the following technical-problem solutions was provided based on this discovery.

The washing art of the substrate concerning invention of the means [I-A] \*\*\*\*\* (1) term which solves a technical problem evaporates washing processing liquid at the temperature of under the boiling point in the method of supplying the steam of washing processing liquid to a substrate, and performing washing processing of a substrate, and it carries out supplying the steam of the generated washing processing liquid to a substrate at the temperature exceeding the dew-point, and carrying out washing processing as the feature.

Various kinds of following things can be used as above-mentioned washing processing liquid.

The mixed liquor of the [I] sulfuric acid ( $\text{H}_2\text{SO}_4$ ), a sulfuric acid, and a hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), the oleum ( $\text{H}_2\text{SO}_4+\text{SO}_3+\text{H}_2\text{O}_2$ ) containing the sulfuric acid of 97 - 98% of concentration, and sulfuric-acid solution -- the steam of these It is effective in removing the organic substance and an inorganic substance, and in the sulfuric-acid solution ( $\text{H}_2\text{SO}_4+\text{H}_2\text{O}$ ) whose boiling point is 317 degrees C in 98.4% of compositions, it reacts with a metal impurity, and becomes a sulfate, and the dissolution removal of the metal impurity can be carried out by it.

[2] a nitric acid ( $\text{HNO}_3$ ), the fuming nitric acid ( $\text{HNO}_3+\text{NO}_2+\text{H}_2\text{O}$ ) containing the nitric acid of 86% or more of concentration, and nitric-acid solution -- the steam of these reacts with a metal impurity, serves as a nitrate, and can carry out dissolution removal of the metal impurity by it However, aluminum (aluminum), chromium (Cr), and iron (Fe) serve as a passive state. Moreover, a silicon front face can be oxidized.

[3] the mixed liquor of a nitric acid ( $\text{HNO}_3$ ) and hydrogen halides (HF, HCl, etc.), and its solution -- the steam of these reacts with a metal impurity and can carry out dissolution removal Moreover, a particle metallurgy group impurity is removable with the combination of the oxidation and the oxide disintegration of a hydrogen halide by the nitric acid.

[4] hydrogen fluoride solution (hydrofluoric acid) ( $\text{HF}+\text{H}_2\text{O}$ ), the mixed liquor of hydrogen fluoride (HF) and alcohol (ROH), and its solution -- the steam of these is effective in etching removal of a natural oxidation film ( $\text{SiO}_x$ ), reacts with a metal impurity, serves as a fluoride and can carry out dissolution removal

[5] the mixed liquor of hydrogen fluoride (HF) and a hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and its solution, the mixed liquor of hydrogen fluoride (HF), alcohol (ROH), and a hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and its solution -- the steam of these disassembles the oxide by the oxidization and hydrogen fluoride on the front face of silicon by the hydrogen peroxide simultaneously, and can remove a particle metallurgy group impurity

[6] hydrogen chloride solution (hydrochloric acid) ( $\text{HCl}+\text{H}_2\text{O}$ ), the mixed liquor of a hydrogen chloride

(HCl) and alcohol (ROH) and its solution, the mixed liquor of a hydrogen chloride (HCl) and a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and its solution, the mixed liquor of a hydrogen chloride (HCl), alcohol (ROH), and a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and its solution -- the steam of these reacts with a metal impurity and can carry out dissolution removal as a chloride

[7] an aqueous ammonia solution (NH<sub>3</sub>+H<sub>2</sub>O), the mixed liquor of ammonia (NH<sub>3</sub>) and alcohol (ROH), and its solution -- the steam of these can remove particle using what ammonia melts a silicon compound for slightly (silicon is \*\*\*\*\*ed)

[8] the mixed liquor of ammonia (NH<sub>3</sub>) and a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and its solution, the mixed liquor of ammonia (NH<sub>3</sub>), alcohol (ROH), and a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and its solution -- the steam of these can remove particle by the silicon etching operation by ammonia, and the oxidation by the hydrogen peroxide After processing, the front face of a substrate can be oxidized and a hydrophilic property can be presented.

[9] A choline ([ (CH<sub>3</sub>)<sub>3</sub>NC<sub>2</sub>H<sub>4</sub>OH] OH) and a choline derivative ([ (C<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>Ns] OH), choline solution ([ (CH<sub>3</sub>)<sub>3</sub>NC<sub>2</sub>H<sub>4</sub>OH] OH+H<sub>2</sub>O), the mixed liquor of a choline ([ (CH<sub>3</sub>)<sub>3</sub>NC<sub>2</sub>H<sub>4</sub>OH] OH) and alcohol (ROH), and its solution -- the steam of these can remove particle by the silicon etching operation by the choline

[10] the mixed liquor of a choline ([ (CH<sub>3</sub>)<sub>3</sub>NC<sub>2</sub>H<sub>4</sub>OH] OH) and a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and its solution, the mixed liquor of alcohol (ROH) with a choline ([ (CH<sub>3</sub>)<sub>3</sub>NC<sub>2</sub>H<sub>4</sub>OH] OH), and a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and its solution -- the steam of these can remove particle by the silicon etching operation by the choline, and the oxidation by the hydrogen peroxide After processing, the front face of a substrate can be oxidized and a hydrophilic property can be presented.

[II-A] The washing art of the substrate concerning invention of a \*\*\*\*\* (2) term is characterized by conveying the substrate which carried out washing processing in a wet washing processing room, supplying washing processing liquid to a substrate, and carrying out washing processing by the above-mentioned method, again.

As washing processing liquid used at a wet washing processing room, you may be not only pure water (deionized water) but ammonia hydrogen peroxide solution, hydrochloric-acid hydrogen peroxide solution, a choline, or a choline derivative etc. Furthermore, you may make it rotate and it is not necessary to rotate a substrate in washing processing at a wet washing processing room.

[III-A] the washing processor of the substrate concerning invention of a \*\*\*\*\* (3) term again When enforcing the washing art of the substrate concerning invention of the above-mentioned \*\*\*\*\* (2) term, as suitable equipment The steam supplied in washing processing liquid from the steamy generation source which evaporates at the temperature of under the boiling point, and the aforementioned steamy generation source The wet washing processing room which carries out washing processing with the steam of the washing processing liquid of the above [ the substrate which has the \*\* tone means which carries out a \*\* tone to the temperature exceeding the dew-point, and was contained inside ] by which the \*\* tone was carried out, The substrate conveyance mechanism in which a substrate [ finishing / washing processing ] is conveyed from the aforementioned dry type washing processing room, The washing processor of the substrate dissociated from the aforementioned dry type washing processing room, and it was prepared, had the supply means of washing processing liquid, and had the wet washing processing [ in which contain the substrate / finishing / washing processing ] conveyed according to the aforementioned substrate conveyance mechanism, supply washing processing liquid, and washing processing is carried out in a substrate / room is proposed.

The operation by the washing art of the substrate concerning generating of a <operation [I-B]> \*\*\*\*\* (1) term is as follows.

As a steam of the washing processing liquid supplied to a substrate for substrate washing processing, at the temperature of under the boiling point of washing processing liquid, evaporated washing processing liquid and generated. Namely, the steam of the washing processing liquid which was evaporated from the front face of washing processing liquid by molecular diffusion-evaporation which tends toward the balance of the mass transfer of a vapor-liquid bi-phase interface, without boiling washing processing liquid, and was generated is supplied. And under the temperature atmosphere which exceeds the dew-



point of the steam of washing processing liquid for the washing processing by the steam of the washing processing liquid, That is, since generation of the aerosol by liquefaction of the steam of washing processing liquid is prevented by carrying out under the conditions from which the maximum vapor tension of the steam of washing processing liquid turns into more than the partial pressure, the cause of generation of colloidal silica will be severed from origin. By making into the temperature exceeding a dew-point temperature of evaporation of the washing processing liquid which carried out evaporation generation of the steam of washing processing liquid, and was generated at the temperature of under a boiling point, generating and liquefaction of aerosol are prevented and it can prevent that pollute a substrate front face by impurities, particle is formed, the particle carried by aerosol adheres, or uneven etching is generated.

In addition, for generation prevention of colloidal silica, since it is important that aerosol (Myst) is not included and the steam itself is a gas, even if this is contained, it does not pose a problem.

The operation by the washing art of the substrate concerning invention of a [II-B] \*\*\*\*\* (2) term is as follows.

Since the substrate after the washing processing by the steam of washing processing liquid is conveyed in a wet washing processing room and washing processing liquid washes Can avoid that the washing processing liquid supplied in the wet washing processing interior of a room mixes into the steam of washing processing liquid, and, moreover, washing processing liquid is not supplied in the shape of a fog. Generation of colloidal silica can be prevented by wearing the whole surface on the front face of a substrate after the washing processing by the steam of washing processing liquid with washing processing liquid.

The operation by the washing processor of the substrate concerning invention of a [III-B] \*\*\*\*\* (3) term is as follows.

At the temperature of under the boiling point of washing processing liquid, the steamy generation source of washing processing liquid evaporated washing processing liquid, and occurred. Namely, it is constituted by what generates the steam of the washing processing liquid which was evaporated from the front face of washing processing liquid by molecular diffusion-evaporation which tends toward the balance of the mass transfer of a vapor-liquid bi-phase interface, without boiling washing processing liquid, and was generated. And it has the \*\* tone means which carries out a \*\* tone to the temperature to which a dry type washing processing room exceeds the dew-point of the steam of washing processing liquid. Since it has prevented the steam of washing processing liquid liquefying in the dry type washing processing interior of a room, and becoming aerosol, a dry type washing processing room is separated from a wet washing processing room. Since it has avoided beforehand that the washing processing supplied in the wet washing processing interior of a room mixes in the steam of the washing processing liquid of the dry type washing processing interior of a room, washing processing by the steam of washing processing liquid can be performed under conditions without generating of aerosol, and generation of colloidal silica is prevented.

and when the substrate by which washing processing was carried out by doing in this way is taken out from a dry type washing processing room according to a substrate conveyance mechanism While compounds, such as a silicon tetrafluoride which may cause colloidal silica generation, secede from the substrate front face, are and it does not remain. And since it is taken out from the aforementioned dry type washing processing room and a silicon tetrafluoride does not contact a substrate newly any longer And since it is high air of the cleanliness kicked to a clean room and aerosol is not included, that a substrate is exposed Generation of colloidal silica is prevented also in this stage, and since washing processing of the whole surface of a substrate is carried out in the state of a wrap with washing processing liquid, generation of colloidal silica is prevented in the wet washing processing interior of a room.

In the washing art of the substrate concerning invention of the \*\*\*\*\* (1) term mentioned above, what does not perform washing processing with washing processing liquid like invention of a \*\*\*\*\* (2) term is included. Because, when performing growth of membrane formation or a natural oxidation film, while forming piping of the reactor core tube of the oxidization furnace, a substrate boat, and a raw

gas etc. with the quality of the material without an impurity When using the thing of the high grade of the nine and 9 (purity is the thing of 99.99999999) grade, as a raw gas further While forming a conveyance mechanism, a chamber, etc. with the quality of the material without an impurity in the washing process before growth of those membrane formation and natural oxidation films As it was called the case where used the thing of a high grade as washing processing liquid, and it transported to the following process in the clean room which it is under the atmosphere of the inert gas of a high grade It is because the quality of a substrate does not deteriorate by accumulation at the process before the washing processing by the steam of washing processing liquid, either, even if it does not perform washing processing with the washing processing liquid in a back process, when there is no particle metallurgy group impurity.

In the washing method of the substrate concerning invention of a \*\*\*\*\* (2) term, and the washing processor of the substrate concerning invention of a \*\*\*\*\* (3) term, although washing processing with washing processing liquid was performed by locus different from the washing processing by the steam of washing processing liquid If washing processing with washing processing liquid is performed in the state where it considered as the dryness atmosphere which replaces the interior of a room by dryness inert gas, and does not contain aerosol after the washing processing by the steam of washing processing liquid, since generation of colloidal silica will not arise, It contains, when performing washing processing by the steam of washing processing liquid, and washing processing with washing processing liquid as a washing art of the substrate concerning invention of a \*\*\*\*\* (1) term in the same interior of a room.

The example of this invention is explained in detail based on a drawing below a <example>.

The 1st example of the 1st example is an example which shows the washing processor of the substrate for enforcing the washing art of the substrate concerning invention of a \*\*\*\*\* (1) term.

A view 1 is a cross section of the 1st example, in this drawing, 1 shows the depot which stores the mixed liquor of hydrofluoric-acid HF and pure water H<sub>2</sub>O, i.e., the washing processing liquid of a false azeotropy state mentioned later, crosses it to the bottom wall section and the side-attachment-wall section of this depot 1, and the piping 3 which infixed the pump 2 for churning is connected.

Moreover, while the washing processing liquid supply pipe 4 from another reservoir tank (not shown) which stores the washing processing liquid (the Morita chemical-industry company make) of a false azeotropy state is connected to a depot 1, it is constituted so that the opening-and-closing valve 5 is infixed in the washing processing liquid supply pipe 4, the opening-and-closing valve 5 may be opened when the reservoir level of washing processing liquid falls rather than the position detected with a level gage 6, and it may supply suitably.

In the depot 1, while the heater 7 which heats washing processing liquid, and the cooling pipe 8 which cools washing processing liquid are formed, the temperature sensor 9 which measures the temperature of the stored washing processing liquid is formed. While a temperature sensor 9 is connected to a temperature controller 10, the solenoid valve 11 and heater 7 which were infixed in the cooling pipe 8 are connected to the temperature controller 10.

A heater 7 and a solenoid valve 11 are controlled by the temperature controller 10 to make it 30 degrees C (for this temperature to be equivalent to 39.4% of false azeotropy concentration under 760mmHg mentioned later) of false azeotropic temperatures which mention the temperature of the washing processing liquid in a depot 1 later based on the detection temperature by the temperature sensor 9, equalizing the temperature of the washing processing liquid currently stored with the pump 2 for churning.

That is, when temperature falls by the supplement of washing processing liquid to a depot 1 etc., it energizes at a heater 7 and the washing processing liquid in a depot 9 is heated, and a temperature up is carried out until it becomes 30 degrees C of false azeotropic temperatures. On the contrary, when 30 degrees C of false azeotropic temperatures are exceeded, a solenoid valve 11 is opened, and cooling water is poured and lowered to a cooling pipe 8.

It is constituted so that the washing processing liquid which is mixed liquor of hydrofluoric-acid HF and pure water H<sub>2</sub>O may be maintained in the false azeotropy state and it may evaporate under in a boiling

point by this temperature control.

While the nitrogen gas supply pipe 14 which infixed the flow regulator 12 and the solenoid valve 13 and which supplies the nitrogen gas N<sub>2</sub> for carriers is connected to a depot 1, nozzle 14a which has a perforated plate is connected at the nose of cam, and the distributed equation of the pressure in the evaporation reservoir section 15 of the upper part in a depot 1 is carried out.

Moreover, the steamy supply pipe 17 which supplies the steam of the washing processing liquid diluted with the nitrogen gas N<sub>2</sub> for carriers from the evaporation reservoir section 15 to the dry type washing processing room 16 is connected to the depot 1.

While the pressure sensor 18 which measures the pressure of the controlled atmosphere containing the steam of the connection processing liquid in the steamy reservoir section 15 of a depot 1 is formed and this pressure sensor 18 is connected to a pressure controller 19 The solenoid valve 13 of the nitrogen gas supply pipe 14 is connected to the pressure controller 19. Based on the pressure measured by the pressure sensor 18, opening-and-closing control of the solenoid valve 13 is carried out, and it is constituted so that the amount of supply of nitrogen gas N<sub>2</sub> may be adjusted and the ambient-pressure force of the steamy reservoir section 15 in a depot 1 may be maintained to atmospheric pressure 760mmHg.

The steamy reservoir section 15 and the steamy supply pipe 17 of a part for the nose-of-cam flank of the nitrogen gas supply pipe 14 and a depot 1 are covered with the outer tube 20 made from a heat insulator, while the upper section and the downstream of this outer tube 20 are connected through the bypass piping 22 which infixed the pump 21, warm water is held in the interior, and the heater 23 is formed in the part while being the bypass piping 22.

By this composition, the warm water warmed by necessary temperature (for example, 50 degrees C) at the heater 23 is circulated. The temperature of the steam of the washing processing liquid which is the hydrogen fluoride gas and the mixed steam of pure water steamy HF/H<sub>2</sub>O which are passed by the steamy supply pipe 17 from the steamy reservoir section 15 is maintained to the temperature exceeding a dew-point. In the steam of the washing processing liquid which hydrogen fluoride gas and the pure water steam mixed, the false azeotropy concentration of the hydrogen fluoride gas under 760mmHg and 30-degree C conditions is maintained to 39.4%.

That is, it has prevented making it become more than each partial pressure, and the steam or each of its component of washing processing liquid condensing namely, liquefying each maximum vapor tension of the steam of the washing processing liquid in atmosphere, and each component of the steam.

In addition, at this time, the sum total (PHF+PH<sub>2</sub>O) of the partial pressure of hydrogen fluoride gas and a pure water steam is 18mmHg(s), and the partial pressure of nitrogen gas N<sub>2</sub> serves as 742mmHg(s).

A view 11 is a vapor pressure view of the mixed liquor of hydrogen fluoride HF and water H<sub>2</sub>O. The partial pressure PHF of hydrogen fluoride HF is taken along a horizontal axis, the total pressure force (PHF+PH<sub>2</sub>O) with total pressure P PHF, i.e., partial pressure of hydrogen fluoride HF, and the partial pressure PH<sub>2</sub>O of steam H<sub>2</sub>O is taken along a vertical axis, and the relation between partial pressure PHF and total pressure (PHF+PH<sub>2</sub>O) is shown by making temperature T into a parameter.

The line of two or more slant is a straight line which shows each composition ratio (mole fraction) of hydrogen fluoride to the whole mixed liquor.

In this drawing, under the conditions mentioned above, if the temperature of the steam generated at 30 degrees C of false azeotropic temperatures is maintained to the temperature exceeding 30 degrees C, hydrogen fluoride gas and the mixed steam of pure water steamy HF/H<sub>2</sub>O will not be condensed namely, liquefied. On the other hand, if the partial pressure of 18mmHg(s) and nitrogen gas makes [ the partial pressure of hydrogen fluoride gas and the mixed gas of a pure water steam ] temperature of the steam with which total pressure consists of 760mmHg(s) lower than 30 degrees C by 742mmHg(s) when the concentration of hydrogen fluoride is 39.4% of false azeotropy concentration mentioned later, the mixed steam of hydrogen fluoride gas and a pure water steam will liquefy.

Since the steam of the washing processing liquid which mixed such hydrogen fluoride gas that does not contain aerosol, and the pure water steam is generated The composition which maintains the temperature of washing processing liquid at 30 degrees C by a heater 7, the cooling pipe 8, the temperature sensor 9,

the temperature controller 10, and the solenoid valve 11, What consists of the composition of maintaining the ambient-pressure force in a depot 1 to 760mmHg(s) corresponds to the row at the steamy generation source said to the composition of invention with the solenoid valve 13, the nitrogen gas supply pipe 14, the pressure sensor 18, and the pressure controller 19.

Here, false azeotropy is explained.

A view 2 shows the property of composition ratio opposite temperature in case the total pressure force (PHF+PH<sub>2</sub>O) of the partial pressure PHF of hydrogen fluoride HF and the partial pressure PH<sub>2</sub>O of water H<sub>2</sub>O is 760mmHg(s), a horizontal axis is the composition ratio (concentration) [%] of hydrogen fluoride HF, and a vertical axis is temperature [\*\*].

In a view 2, the liquidus line and the vapor line of 760mmHg(s) of hydrogen fluoride HF and water H<sub>2</sub>O meet at the temperature of 111.4 degrees C. [ of mixed liquor ] Although this is the azeotropic point, the concentration of hydrogen fluoride HF in the azeotropic point is 37.73%.

The washing processing liquid which becomes a depot 1 from hydrofluoric-acid HF of 37.73% of concentration and  $100-37.73=62.27\%$  pure water H<sub>2</sub>O is stored. If the ambient-pressure force of a depot 1 is maintained at 760mmHg(s) and the temperature of washing processing liquid is kept at 111.4 degrees C Azeotropy conditions are fulfilled, the composition ratio of the steam of washing processing liquid is set to the HF:H<sub>2</sub>O=37.73:62.27 [ same ] as washing processing liquid, and even if the amount of washing processing liquid decreases with advance of evaporation, the composition ratio is always maintained uniformly.

However, since the temperature of 111.4 degrees C is comparatively high and safety is increased, it is desirable to evaporate washing processing liquid at low temperature more. In the pressure (PHF+PH<sub>2</sub>O) which fulfills azeotropy conditions, the concentration of 18mmHg(s) and hydrofluoric-acid HF becomes 39.4% to make evaporation temperature into 30 degrees C. = (PHF+PH<sub>2</sub>O) Although 18mmHg must be decompressed to consider as ambient gas pressure, it is false azeotropy to needlessness-ize the reduced pressure and to make it evaporate under the atmosphere of atmospheric pressure 760mmHg.

That is, the washing processing liquid which mixed 39.4% of hydrofluoric-acid HF and  $100-39.4=60.6\%$  pure water H<sub>2</sub>O is supplied in a depot 1, and a heater 7, a cooling pipe 8, a temperature sensor 9, and a temperature controller 10 perform temperature control so that the temperature of the washing processing liquid may be maintained at 30 degrees C.

And the ambient-pressure force which totaled the partial pressure PHF, PH<sub>2</sub>O, and PN<sub>2</sub> of a steam, the controlled atmosphere, i.e., the hydrogen fluoride gas, in a depot 1, and nitrogen gas carries out the evaporation evaporation of the washing processing liquid in the state of 760mmHg(s). When ambient gas pressure shifts from 760mmHg(s), pressure regulation is performed so that 760mmHg(s) may be maintained with a pressure sensor 18, a solenoid valve 13, and a pressure controller 19.

That is, the nitrogen gas N<sub>2</sub> of the partial pressure of  $760-18=742\text{mmHg}$  is supplied to a depot 1 as a controlled atmosphere-cum-carrier gas through the nitrogen gas supply pipe 14.

The composition ratio of the washing processing liquid in this case is HF:H<sub>2</sub>O=39.4:60.6. On the other hand, when the composition ratio of a controlled atmosphere is calculated, it is HF:H<sub>2</sub>O:N<sub>2</sub>=5.21:8.00:86.79 (however, the above-mentioned proportional expression is expressed as HF+H<sub>2</sub>O+N<sub>2</sub>=100.). In addition, in expression made into HF+H<sub>2</sub>O+N<sub>2</sub>=760, it is expressed as HF:H<sub>2</sub>O:N<sub>2</sub>=7.09:10.91:742.

It is different from the composition ratio of a next door and washing processing liquid.

However, not the composition ratio in the whole controlled atmosphere but the composition ratio between hydrogen fluoride gas HF and steam H<sub>2</sub>O is important for washing processing of Substrate W. This composition ratio is HF:H<sub>2</sub>O=5.21:8.00=39.4:60.6 (even the case of expression made in addition into HF+H<sub>2</sub>O+N<sub>2</sub>=760 HF:H<sub>2</sub>O=7.09:10.91=39.4:60.6).

It comes out, and it is and this is in agreement with the composition ratio in washing processing liquid. This is false azeotropy.

Therefore, the composition ratio of the steam of the washing processing liquid supplied to the dry type washing processing room 16 explained below is always maintained uniformly. And generating of the steam of washing processing liquid is attained in atmospheric pressure and the low temperature of 30

degrees C, and while safety is raised, there is no need for reduced pressure.

Moreover, since it is made to evaporate from a liquid front face in order to evaporate washing processing liquid at the temperature of under the boiling point of washing processing liquid, without boiling washing processing liquid, that it is more important for this invention does not have generating of aerosol.

Next, the structure of the dry type washing processing room 16 is explained.

The mechanical chuck 25 which holds and carries out level rotation of the substrates W, such as a semiconductor wafer, is formed in the interior of the cylinder-like-object-with-base-like substrate processing room 24. The chuck holding the substrates W, such as a wafer, may be a vacuum adsorption chuck of not only a mechanical chuck but well-known technology. Moreover, you may be the chuck which installed inside a heating means to heat a substrate to necessary temperature, carrying out vacuum adsorption. It is constituted so that interlocking connection of the electrical motor 27 may be carried out at the axis of rotation 26 of the mechanical chuck 25 and drive rotation of the substrate W held by the mechanical chuck 25 may be carried out by the circumference of the vertical-axis heart.

The wrap cup-like lid 28 consists of the taper peripheral wall section, a chamber 29 united with the pars basilaris ossis occipitalis in the watertight state, and a top plate united with the upper part in the watertight state in upper part opening of the substrate processing room 24. the constant temperature which the warm water supply tube 30 and the warm water eccrisis tube 31 for making the warm water of constant temperature (for example, 50 degrees C) pile up in the interior of a lid 28 in always are connected to the taper peripheral wall section, and maintains the temperature inside a lid 28 to constant temperature -- it is constituted by \*\*\*\* 32

An aspirator 33 is formed in the interior of \*\*\*\* 32. constant temperature -- to the aspirator 33 The steamy supply pipe 17 which supplies the steam of the washing processing liquid with which the hydrogen fluoride-gas HF for etching and washing the front face of Substrate W, pure water steamy H<sub>2</sub>O, and nitrogen gas N<sub>2</sub> were mixed, The carrier gas supply tube 34 which supplies the nitrogen gas N<sub>2</sub> as carrier gas, The steamy supply tube 35 which supplies the steam of washing processing liquid to a chamber 29 is connected. It is constituted so that the steam of the washing processing liquid diluted while attracting the steam of washing processing liquid and diluting the steam of washing processing liquid with carrier gas N<sub>2</sub> with the negative pressure produced with a flow in a flow of carrier gas N<sub>2</sub> may be supplied to a chamber 29.

the steamy supply pipe 17, an aspirator 33, and the steamy supply tube 35 -- constant temperature -- it has inserted into \*\*\*\* 32 for carrying out the \*\* tone of the steam of washing processing liquid to the temperature exceeding a dew-point, and preventing the liquefaction, i.e., generating of aerosol this meaning -- constant temperature -- what consists of the outer tube 20, the pump 21 and the bypass piping 22 which perform the \*\* tone to a \*\*\*\* 32 side and the depot 1 side of the washing processing liquid of the steamy supply pipe 17, and a heater 23 corresponds to the \*\* tone means said to the composition of invention

A chamber 29 has the gas-stream entrance which inclined at the suitable angle (for example, 30 degrees) to the direction of a path in the peripheral wall section, and the perforated plate 36 is formed in lower part opening. The steam of the washing processing liquid which flowed from the inclination gas-stream entrance in the chamber 29 serves as a vortex within a chamber 29, by the centrifugal operation, there are many flow rates as a periphery and a flow rate decreases as a core. Therefore, in the idle state of the mechanical chuck 25, the outflow discharge of the steam of the washing processing liquid from the stoma of a perforated plate 36 increases like a periphery. By this, if the mechanical chuck 25 rotates, a horizontal air current will occur, negative pressure is produced, the outflow discharge from a core side is increased to a core side, the outflow discharge from all the stomata of a perforated plate 36 is equated, and the steam of washing processing liquid can be uniformly supplied now to the front face of Substrate W.

The cup-like lid 28 is constituted free [ vertical movement ] with a chamber 29, by descent, contacts the packing of the upper limb of the substrate processing room 24, and airtight-izes the substrate processing room 24. The pneumatic cylinder 37 for rise and fall is formed as a mechanism which moves a lid 28 up

and down.

The main processing section which consists of lid 28 grade of the shape of the substrate processing room 24 and a cup explained above is covered with housing 38, and has double room structure. In the part equivalent to the height position of the mechanical chuck 25, carrying-in mouth 38a of a substrate and taking-out mouth 38b are formed in housing 38, and it is opened and closed by the shutter which is not illustrated.

On the outside of housing 38, while the substrate conveyance mechanism 39 of an expansion-and-contraction arm formula is formed in the position near carrying-in mouth 38a In the state where the substrate conveyance mechanism 40 of an expansion-and-contraction arm formula was formed also in the position near taking-out mouth 38b, went up the lid 28, and the substrate processing room 24 is opened wide Where adsorption maintenance of the substrate W is carried out, while carrying in Substrate W in housing 38 through carrying-in mouth 38a It is constituted so that Substrate W may be transferred to the mechanical chuck 25 and Substrate W may be taken out from the mechanical chuck 25 to the housing 38 shell exterior through taking-out mouth 38b. About the structure of these substrate conveyance mechanisms, it is indicated by JP,60-176548,U, for example.

41 shows the exhaust pipe of the substrate processing room 24, and 42 shows the exhaust pipe of housing 38, respectively.

Operation, next operation of the washing processor of the substrate of the above-mentioned composition are explained.

discharging the warm water which supplies the warm water of constant temperature (50 degrees C) from the warm water supply tube 30, and is cooled by the heat exchange at the dry type washing processing room 16 from the warm water eccrisis tube 31 -- constant temperature -- the temperature in \*\*\*\* 32 is maintained uniformly

Carrying-in mouth 38a is opened, a pneumatic cylinder 37 is expanded, a lid 28 is raised, and the space where the substrate conveyance mechanism 39 can advance between a lid 28 and the mechanical chuck 25 is secured. And lay Substrate W in the substrate conveyance mechanism 39, and Substrate W is made to hold by vacuum suction, after carrying in Substrate W in housing 38 from carrying-in mouth 38a and transferring to the mechanical chuck 25 by carrying out the extension drive of the substrate conveyance mechanism 39, carry out refraction operation of the substrate conveyance mechanism 39, it is made to evacuate from carrying-in mouth 38a, and carrying-in mouth 38a is blockaded.

A pneumatic cylinder 37 is shrunk, a lid 28 is dropped, a pressure welding is carried out to the substrate processing room 24, and the substrate processing room 24 is sealed. Subsequently, Substrate W is rotated with the mechanical chuck 25 by driving an electrical motor 27. And negative pressure is generated by feeding carrier gas N<sub>2</sub> into an aspirator 33 through the carrier gas supply tube 34. Then, the steam of the washing processing liquid with which the hydrogen fluoride gas HF and pure water steamy H<sub>2</sub>O which do not contain the aerosol by which the composition ratio was uniformly maintained through the steamy supply pipe 17 from the steamy reservoir section 15 of a depot 1, and nitrogen gas N<sub>2</sub> were mixed is attracted by the aspirator 33. In addition, even if it does not use an aspirator 33, the steam of washing processing liquid flows into a chamber 29.

With the warm water through which the steam of the washing processing liquid which flows the steamy supply pipe 17 circulates with a pump 21 at this time while being heated at a heater 23 It is maintained by the necessary temperature exceeding the dew-point of the steam of washing processing liquid, and the liquefaction is prevented. moreover, the steam of the washing processing liquid with which an aspirator 33 and the steamy supply tube 35 flow each the nose-of-cam side of the steamy supply pipe 17 -- the constant temperature inside the cup-like lid 28 -- the liquefaction is prevented by the warm water of \*\*\*\* 32, and generation of aerosol is prevented

The steam of the washing processing liquid which was mixed with carrier gas N<sub>2</sub> and diluted with the aspirator 33 is supplied in a chamber 29 from the gas-stream entrance which inclined through the steamy supply tube 35.

The steam of the washing processing liquid aslant injected in the chamber 29 serves as a vortex in a chamber 29, and it is supplied to Substrate W through a perforated plate 36, there being many flow rates



as a periphery and circulating through a core in the state with few flow rates. The air current which goes to the method of the outside of radial with the centrifugal force accompanying rotation of the mechanical chuck 25 occurs.

By defining suitably the supply flow rate of the steam of washing processing liquid, and the rotational speed of the mechanical chuck 25, it will act on Substrate W by the uniform air current by balance of negative pressure generating by the air current accompanying a centrifugal force, and the air current which flows down from a perforated plate 36. By this, in Substrate W, etching processing to a silicon thermal oxidation film can be carried out to homogeneity over the whole surface, and the profile becomes flat.

In addition, by performing the \*\* tone which the steam of the washing processing liquid which does not contain aerosol is supplied [ tone ], and does not make aerosol generate on the way, in the etching processing to Substrate W, where generation of colloidal silica is refused from origin, it can

\*\*\*\*\*

After necessary etching is completed, while stopping supply of the steam of washing processing liquid, an electrical motor 27 is stopped, and the inside of the substrate processing room 24 and housing 38 is purged through exhaust pipes 41 and 42. And a pneumatic cylinder 37 is expanded, a lid 28 is raised, and the substrate processing room 24 is opened. Taking-out mouth 38b is opened, extension operation of the substrate conveyance mechanism 40 is carried out, Substrate W is received, and Substrate W is taken out outside through taking-out mouth 38b by refraction operation. And taking-out mouth 38b is blockaded.

The 2nd example of the 2nd example is for enforcing the washing art of the substrate concerning invention of a \*\*\*\*\* (2) term, and is an example which shows the washing processor of the substrate concerning invention of a \*\*\*\*\* (3) term.

A view 3 is a cross section of the 2nd example, the dry type washing processing room 16 is adjoined, the wet washing processing room 60 is formed, and it carries in the substrate W after carrying out washing processing with the steam of washing processing liquid according to the substrate conveyance mechanism 40, and it is constituted so that the washing processing with washing processing liquid may be carried out.

The dry type washing processing room 16 is a thing as explained previously, and omits the explanation by attaching the same drawing number.

Next, the wet washing processing room 60 is explained.

The spin chuck 63 in which drive rotation is carried out by the electrical motor 62 where suction maintenance of the substrate W is carried out into the washing processing tub 61, The nozzle 64 which injects pure water H<sub>2</sub>O to Substrate W, and the nozzle 65 which injects washing lotion liquid, While preventing spilling of the injected pure water or the medical fluid, the covering 66 which smooths flowing down is formed, and the pneumatic cylinder 67 of the washing processing tub 61 which goes up and down covering 66 is formed caudad. Nozzles 64 and 65 are constituted by the respectively cylindrical capillary nozzle.

The composition which consists of the nozzle 64 which injects pure water H<sub>2</sub>O to Substrate W, and the nozzle 65 which injects washing lotion liquid is equivalent to the supply means of the washing processing liquid said to the composition of invention.

68 -- a pure water depot and 69 -- in the pump and 72, an exhaust pipe and 73 show the drainage tube and 74 shows [ the pump and 70 / a medical fluid depot and 71 ] the substrate conveyance mechanism of an expansion-and-contraction arm formula, respectively In addition, as washing processing liquid, although the mixed liquor of pure water and washing lotion liquid is used, as the washing lotion liquid, the selection use of ammonia hydrogen peroxide solution, hydrochloric-acid hydrogen peroxide solution, a choline, or the choline derivative can be carried out.

Since it is in the high clean room of cleanliness that Substrate W is placed [ which is volatilizing steadily from the front face of Substrate W ] and the silicon tetrafluoride SiF<sub>4</sub> constituting the cause of generation of colloidal silica does not contain aerosol, generation of colloidal silica is prevented, until it carries in to the wet washing processing room 60 according to this 2nd example, after taking out the

substrate [ finishing / etching ] W to the exterior of the dry type washing processing room 16.

Moreover, the dry type washing processing room 16 is separated from the wet washing processing room 60, the washing processing liquid injected at the wet washing processing room 60 serves as Myst, and it does not invade in the substrate processing room 24.

Therefore, good etching without remains adhesion of particle can be performed.

Operation, next operation at the wet washing processing room 60 in this 2nd example are explained.

At the wet washing processing room 60, open carrying-in mouth 61a in the state where covering 66 was descended by contraction of a pneumatic cylinder 67, transfer the substrate W after washing processing was carried out by the steam of washing processing liquid at the dry type washing processing room 16 on a spin chuck 63 according to the substrate conveyance mechanism 40, the substrate conveyance mechanism 40 is made to leave, and carrying-in mouth 61a is closed. And after elongating a pneumatic cylinder 67 and raising covering 66, first, a pump 70 is driven, washing lotion liquid, such as a choline, is supplied to Substrate W from a nozzle 65, primary washing is performed, subsequently a pump 68 is driven, pure water is supplied to Substrate W from a nozzle 64, and secondary washing is performed. In this case, since nozzles 64 and 65 are cylindrical capillary nozzles, the raise in basic wages silicon front face of Substrate W can be completely covered with a medical fluid and pure water at a stretch, and generation of colloidal silica is prevented.

Since covering 66 is the smooth thing which promotes flowing down of washing processing liquid, it is prevented by covering 66 that waterdrop and a drop remain, the effluent of washing processing liquid is discharged good through the drain tube 73, and it prevents that liquid remains in the washing processing tub 61. Moreover, it has prevented that Myst of the internal surface of the washing processing tub 61 adheres to Substrate W by covering Substrate W with covering 66.

If necessary washing considers as an end, by purging the inside of the washing processing tub 61 through the exhaust air tube 72, and carrying out high-speed rotation of the spin chuck 63, the washing processing liquid adhering to Substrate W will be shaken off, and Substrate W will be dried.

After dryness is completed, covering 66 is lowered and the substrate [ finishing / washing ] W is taken out out of a tub according to the substrate conveyance mechanism 74 through taking-out mouth 61b.

In addition, in the time zone which does not wash Substrate W, since a possibility that the bacterium leading to particle may occur is in pure water within piping which leads to a nozzle 64 and it, it is desirable by making pure water flow out of a nozzle 64 in always to prevent generating of a bacterium.

The 3rd example this invention person conducted the experiment which investigates the situation of generation of the particle by organic substance contamination apart from the previous experiment.

Consequently, when there was organic substance contamination, it became clear that it is very advantageous on prevention of colloidal silica generation to remove it beforehand.

#### [Experiment]

As shown in a view 7, the silicon wafer W was put on the vertical posture, the mixed steam (HF/H<sub>2</sub>O) which consists of hydrogen fluoride HF and pure water H<sub>2</sub>O towards a lower shell top was supplied to the front face of a silicon wafer W, and the situation of etching of silicon thermal oxidation film th-SiO<sub>2</sub> on the front face of a silicon wafer was investigated. Since lower one of an etching rate is higher than the upper part, raise in basic wages silicon Si exposes it from the lower part. The boundary of raise in basic wages silicon and a thermal oxidation film goes up in order like e-f, g-h, and i-j to c-d from a-b, and the pan, and, finally a thermal oxidation film is lost. The reaction at this time is  $6\text{HF} + \text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$ . ..... It goes on by \*\*. H<sub>2</sub>SiF<sub>6</sub> is a hexafluorosilicic acid. Water (liquid) is generated in this process. As shown in an octavus view, this generated water gathers in the boundary of raise in basic wages silicon Si and thermal oxidation film th-SiO<sub>2</sub>, serves as waterdrop, and goes up with advance of etching.

In this process, if organic substance contamination is shown in the front face of a thermal oxidation film, or if the travelling direction of etching is not fixed, some thermal oxidation films will be left in the shape of an island, and waterdrop will be left by the boundary of the thermal oxidation film of the shape of the island, and raise in basic wages silicon.

The left waterdrop contains hexafluorosilicic-acid H<sub>2</sub>SiF<sub>6</sub>, and is  $\text{H}_2\text{SiF}_6 \rightarrow \text{SiF}_4 + 2\text{HF}$ . .....



**\*\* $3\text{SiF}_4 + 4\text{H}_2\text{O}_2 \rightarrow \text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{SiF}_6$  ...** It reacts like **\*\*** and colloidal silica  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  is generated on raise in basic waxes silicon in the circumference of waterdrop.

Therefore, in order to prevent generation of colloidal silica, it needs to be cautious of removal of organic substance contamination of a thermal oxidation film front face, and fixation of etching travelling direction.

In the 1st example, travelling direction of etching can be regularity-ized by generating negative pressure by rotation of the mechanical chuck 25 in a core so that a periphery may make [ many ] outflow discharge from a perforated plate 36 by flowing a mixed steam from the gas-stream entrance which inclined to the chamber 29 and it may balance with this, and making outflow discharge from a perforated plate 36 into an equal distribution state as a result. Therefore, organic substance contamination poses a problem.

It is known that washing by UV irradiation and ozone supply is effective in removal of organic substance contamination. Then, as shown in a view 9, while countering the dry type washing processing room 16 of the 1st example, inserting the substrate conveyance mechanism 39 and forming ultraviolet rays and the ozone UV/O<sub>3</sub> washing room 80 as the 3rd example, the substrate conveyance mechanism 81 in which Substrate W was carried in was formed in this ultraviolet rays and ozone UV/O<sub>3</sub> washing room 80.

For 82, as for an ozone injection nozzle and 84, a ultraviolet ray lamp and 83 are [ a spin chuck and 85 ] electrical motors.

Other composition is the same as that of the 1st example and the 2nd example.

Before carrying in Substrate W to the dry type washing processing room 16, at the UV/O<sub>3</sub> washing room 80, organic substance contamination is removed from Substrate W. By this, it is lost that waterdrop is left by the raise in basic waxes silicon side in the shape of an island because of organic substance contamination, and generation of colloidal silica can be prevented in etching / washing processing.

The 4th example of the 4th example is for preparing the washing processing liquid which consists of hydrofluoric-acid HF of 37.73% of concentration, and  $100 - 37.73 = 62.27\%$  pure water H<sub>2</sub>O.

The hydrofluoric-acid depot 101 which a view 10 is a cross section of the 4th example, and contained the solution of hydrofluoric-acid HF of about 50% of commercial concentration as a hydrogen halide for washing processing, The nitrogen gas supply pipe 102 and bulb 103 which feed the nitrogen gas N<sub>2</sub> for sending out a hydrofluoric acid from this hydrofluoric-acid depot 101, The hydrofluoric-acid supply means 106 is constituted with the hydrofluoric-acid supply pipe 104 which supplies a hydrofluoric acid, and the solenoid valve 105 by which it was placed between these hydrofluoric-acid supply pipes 104. Moreover, the pure water supply means 111 consists of a pure water depot 107 which contained pure water H<sub>2</sub>O, and this depot 107 with the pump 108 which feeds pure water, the pure water supply pipe 109 which supplies pure water, and the solenoid valve 110 by which it was placed between these pure water supply pipes 109.

The washing processing liquid depot 112 which stores the washing processing liquid which accepted hydrofluoric-acid HF and pure water H<sub>2</sub>O, and was mixed is formed, and the hydrofluoric-acid supply pipe 104 and the pure water supply pipe 109 are connected to this washing processing liquid depot 112. Moreover, the bypass piping 114 which infixed the pump 113 for churning is connected to the washing processing liquid depot 112, and it is constituted so that churning mixture of hydrofluoric-acid HF and the pure water H<sub>2</sub>O may be carried out.

Moreover, the concentration sensors 115 which detect the concentration of the connection processing liquid stored there to the connection processing liquid depot 112, such as a conductivity meter and an ultrasonic concentration meter, Each is connected to the supply control unit 118. the upper case level sensor 116 and the lower-berth level sensor 117 prepare -- having -- the concentration sensor 115, the upper case level sensor 116, and the lower-berth level sensor 117 -- To the supply control unit 118, the solenoid valve 105 of the hydrofluoric-acid supply pipe 104, A pump 108, the solenoid valve 110 of the pure water supply pipe 109, and the solenoid valve 120 infixed in the drain pipe 119 of the washing processing liquid depot 112 are connected. by these composition Each amount of supply is controlled.

the concentration detected by the concentration sensor 115 -- being based -- hydrofluoric-acid HF and pure water H<sub>2</sub>O -- The concentration management tool 17 is constituted so that the concentration of hydrofluoric-acid HF in the washing processing liquid stored by the washing processing liquid depot 112 may be maintained to 39.4% (this numeric value is an example) of false azeotropy concentration. That is, a pressure is put on the hydrofluoric-acid depot 101 by opening a solenoid valve 103 and feeding nitrogen gas N<sub>2</sub> through the nitrogen gas supply pipe 102. At this time, the solenoid valve 105 is opened and hydrofluoric-acid HF is supplied to the washing processing liquid depot 112 through the hydrofluoric-acid supply pipe 104. If hydrofluoric-acid HF reaches the lower-berth level sensor 117, the supply control unit 118 closes a solenoid valve 105, stops supply of hydrofluoric-acid HF, subsequently, will drive a pump 108 and will supply pure water H<sub>2</sub>O to the washing processing liquid depot 112 through the pure water supply pipe 109 from the pure water depot 107 while it opens a solenoid valve 110.

Here, since the pump 113 for churning is driving, hydrofluoric-acid HF and pure water H<sub>2</sub>O are mixed. If the concentration sensor 115 detects 39.4% of false azeotropy concentration at this time, the supply control unit 118 will suspend a pump 108, and will stop supply of pure water H<sub>2</sub>O while it closes a solenoid valve 110.

Pure water H<sub>2</sub>O is supplied until it opens the solenoid valve 120 for drains, it discharges a part of washing processing liquid and it becomes 39.4% of false azeotropy concentration, when the upper case level sensor 116 turns on, before the concentration sensor 115 detects 39.4% of false azeotropy concentration.

It will take fixed time, before becoming uniform concentration over the whole washing processing liquid until the influence of the heat of dilution is lost and since heat of dilution occurs when hydrofluoric-acid HF and pure water H<sub>2</sub>O are mixed in the washing processing liquid depot 112. When the fixed time passes, a state will be stabilized and washing processing liquid of 39.4% of false azeotropy concentration will be obtained.

The washing processing liquid supply pipe 4 explained in the 1st example is connected to the washing processing liquid depot 112.

Moreover, while the carrier gas supply pipe 122 which supplies the nitrogen gas N<sub>2</sub> as carrier gas is connected to the washing processing liquid depot 112, the solenoid valve 123 is infixed in the carrier gas supply pipe 122. Furthermore, the pressure sensor 124 which measures the pressure in up space to the washing processing liquid depot 112 is formed.

By this composition, a solenoid valve 123 is opened, the nitrogen gas N<sub>2</sub> as carrier gas is sent into the washing processing liquid depot 112 through the carrier gas supply pipe 122, and the washing processing liquid made into predetermined concentration is sent into a depot 1 through the washing processing liquid supply pipe 4. When [ at this time ] it sends and \*\* performs opening-and-closing control of a solenoid valve 123 with the detection pressure of a pressure sensor 124, it is made to become 1 constant pressure.

In the above-mentioned example, although washing processing and dryness processing of Substrate W were performed at the same processing room 60, you may prepare the locus only for dryness processings independently.

Moreover, although it constituted from an above-mentioned example so that etching processing and washing processing of Substrate W might be performed at the separate processing rooms 16 and 60, as long as perfect dryness is realizable after washing processing, you may be made to perform etching processing and washing processing in the same processing interior of a room. That is, it is because there will be no generation of colloidal silica if the conditions of a bone dry are fulfilled in etching processing. However, it is more efficient for time most for changing into a bone-dry state to separate the processing rooms 16 and 20 from this thing.

Moreover, the composition that a substrate is immersed for example, in pure water H<sub>2</sub>O other than composition of injecting pure water H<sub>2</sub>O to a substrate like the washing processing tub 61 is sufficient as the wet washing processing room 60.

According to the washing art of the substrate concerning invention of a <effect-of-the-invention [I-C]>

\*\*\*\*\* (1) term, the following effect is demonstrated.

Can obtain in the state where aerosol is not included for the steam of the washing processing liquid for substrate washing processing by evaporation at the temperature of under the boiling point of washing processing liquid, and, moreover, the steam of the washing processing liquid under the atmosphere of the temperature exceeding a dew-point Since a substrate is supplied in the state where it does not liquefy, the cause of generation of the colloidal silica resulting from aerosol can be severed from origin. While being able to perform washing processing of the substrate by the steam of washing processing liquid good and being able to obtain the substrate of the clean surface, when being accompanied by etching, there is no impurity and uniform etching can be performed.

According to the washing art of the substrate concerning invention of a [II-C] \*\*\*\*\* (2) term, the following effect is demonstrated.

The washing processing with the washing processing liquid to the substrate which carried out washing processing in the above-mentioned method with the steam of the washing processing liquid which does not contain aerosol Since it carries out by conveying in a wet washing processing room, mixing of the washing processing liquid to the inside of the steam of washing processing liquid and generation of the colloidal silica by the washing processing with washing processing liquid itself can be prevented. When performing washing by the steam of washing processing liquid, and washing with washing processing liquid to a series, while being able to obtain the substrate of the clean surface, when being accompanied by etching, there is no impurity and uniform etching can be performed. Therefore, it becomes the bottom of the condition to which remains particle exists after the washing processing by the steam removable [ these remains particle ].

According to the washing processor of the substrate concerning invention of a [III-C] \*\*\*\*\* (3) term, the following effect is demonstrated.

The temperature of the steam of the washing processing liquid is maintained to the temperature which exceeds a dew-point by the \*\* tone means excluding aerosol in the steam of the washing processing liquid generated in a steamy generation source. And since it is considering that separate a dry type washing processing room from a wet washing processing room, and washing processing liquid mixes in the steam of the washing processing liquid of the dry type washing processing interior of a room as the composition avoided beforehand, the washing processing by the steam of washing processing liquid can be carried out under conditions without aerosol.

And at a wet washing processing room, since washing processing of the whole surface of a substrate is carried out in the state of a wrap with washing processing liquid, generation of colloidal silica can be prevented.

The washing processor which performs washing processing good without generation of colloidal silica according to the above synergistic effect to perform washing by the steam of washing processing liquid and washing with washing processing liquid to a series has been offered.

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[Translation done.]

## \* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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**CLAIMS**


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[Claim(s)]

[Claim 1] The washing art of the substrate characterized by supplying the steam of the washing processing liquid which washing processing liquid was evaporated at the temperature of under the boiling point, and was generated in the method of supplying the steam of washing processing liquid to a substrate, and performing washing processing of a substrate to a substrate at the temperature exceeding the dew-point, and carrying out washing processing.

[Claim 2] The washing art of the substrate characterized by conveying the substrate which carried out washing processing in a wet washing processing room, supplying washing processing liquid to a substrate, and carrying out washing processing by the method given in a \*\*\*\*\* (1) term.

[Claim 3] The washing processor of a substrate characterized by providing the following. The steamy generation source which evaporates washing processing liquid at the temperature of under the boiling point. The dry type washing processing room which carries out washing processing with the steam of the washing processing liquid of the above [ the substrate which has the \*\* tone means which carries out the \*\* tone of the steam supplied from the aforementioned steamy generation source to the temperature exceeding the dew-point, and was contained inside ] by which the \*\* tone was carried out. The substrate conveyance mechanism in which a substrate [ finishing / washing processing ] is conveyed from the aforementioned dry type washing processing room. Wet washing processing [ in which it dissociates from the aforementioned dry type washing processing room, is prepared, have the supply means of washing processing liquid, contain the substrate / finishing / washing processing ] conveyed according to the aforementioned substrate conveyance mechanism, supply washing processing liquid, and washing processing is carried out in a substrate / room.

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[Translation done.]